Impact of Well Stimulation on Coal Porosity of Malaysian Coals for Coalbed Methane (CBM) Study

by

Amira Raihana bt Abdul Khalil

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Petroleum Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(PETROLEUM ENGINEERING)

Approved by,

_____

(Mr Saleem Qadir Tunio)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2013

CERTIFICATION OF ORIGINALITY

This is to verify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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AMIRA RAIHANA BT ABDUL KHALIL

ABSTRACT

Coalbed methane (CBM) is an unconventional gas contained in coalbed reservoir. The character of this reservoir is fundamentally different to conventional gas plays because coal is almost pure carbon. Coalbed methane (CBM) wells usually have higher production rate at the beginning of methane production but over time it decreases until it reaches unprofitable level. Well stimulation is one way to solve this problem and this research studies acidizing technique for stimulating coalbed reservoir since there is lack of research done in acidizing of CBM reservoir. The main objective of this research is to observe the effect on porosity of Malaysian coals (still not declared as a CBM producer) before and after being stimulated by different acids that are sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3). Several laboratory tests are performed to determine the porosity. The experiment starts by drying the coal samples in the oven for two hours and the weight for each sample is noted. Each sample is immersed in different acids with different volumes at constant temperature. After immersing the coal samples in acids for six hours, the samples are taken out for weight measurement. The experiment is repeated with different oven temperatures (50^0C and 100^0C) for drying purposes. Upon completion of this research, a higher porosity is expected to be seen on Malaysian coal samples after acidizing job is done. So, it means that different acids have different effects on coal porosity value.

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ABBREVIATIONS AND NOMENCLATURES

CBM	Coalbed methane
FYP	Final year project
GACU	Gad adsorption column unit
HCl	Hydrochloric acid
H_2SO_4	Sulfuric acid
HNO_3	Nitric acid

CHAPTER 1
INTRODUCTION

1.1 BACKGROUND OF STUDY

Malaysian energy sector had been dependent mostly on oil. The government called for the diversification of energy resources away from oil to develop more hydropower and to use more natural gas and coal because of the possibility of prolonged energy crisis faced in the country. (Mohamed & Lee, 2004)

Coal mining history in Malaysia has started since 1851. The current coal resources in Malaysia stands at about 1050 million tones of various types of coal rank, from lignite to anthracite. However, most of them are bituminous and sub-bituminous coal. The majority of coal reserves in Malaysia are found in Sarawak at about 69%, another 29% are found in Sabah, and the remaining 2% are found in Peninsular Malaysia. (Mohamed & Lee, 2004)

Coalbed methane has not been produced in Malaysia eventhough a significant amount of coal resource is identified in the states of Sarawak and Sabah. Based on the preliminary study made on Balingian coal field in Sarawak, it is a very good potential to produce first coalbed methane in Malaysia. (Kong et al., 2011)

Coalbed methane (CBM) is an unconventional gas obtained from coalbed reservoir. The character of this reservoir is fundamentally different to conventional gas plays because coal is almost pure carbon. Special completion, stimulation and production techniques are required to achieved economic production. CBM is extracted by drilling a well into a coal seam. Coal seams are often stimulated to make the CBM flow more freely. (Alberta Energy)

Well stimulation in Oilfield Glossary is defined as "a treatment performed to restore or enhance the productivity of a well". Fracturing and acidizing are the two main types of operations. Highly conductive flow path between the reservoir and the wellbore created by performing the fracturing treatments above the fracture pressure of the reservoir formation. Acidizing treatments are generally designed to restore the natural permeability of the reservoir and it is performed below the reservoir fracture pressure. (Oilfield Glossary)

The most common form of completion/stimulation of coalbeds is hydraulic fracturing, although some adaptions have certainly been made, it is not fundamentally different from fracturing of conventional formations (Palmer, 1992). On the other hand, there is not much research done on acidizing technique to stimulate coal seams.

This project is focussed to study the impact of acidizing technique on coal.

1.2 PROBLEM STATEMENT

Many coalbed methane (CBM) wells initial rates were very encouraging but over time decreased to a level where they would have been uneconomic. One of the solutions to this problem is well stimulation.

Although CBM study is new in oil and gas industry, there is technique that has been successfully used such as hydraulic fracturing stimulation in coalbed reservoir. It is not easy to find successful stories regarding acidizing technique for coalbed reservoir and there is not much research done regarding this technique.

Therefore, this research is one of the initiatives to investigate acidizing technique for stimulating coalbed reservoir to optimize coalbed methane production.

1.3 OBJECTIVE

The main objective of this research is to observe the effect of acid on porosity of Malaysian coals before and after being stimulated by different acids (i.e. sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3)).

Some parameters will be taken into account such as the temperature, volume of acids and sorption capacity.

- Two degrees of temperature (50^{o}C and 100^{o}C) will be used to analyze at which temperature is good for drying the coal samples.
- The volume of each acid varies from 5ml to 25ml to identify which volume can gives better stimulation to the coal samples.
- The sorption capacity will be noted to observe the capability of coal sample to adsorb and desorb methane gas before and after being stimulated by acids.

1.4 SCOPE OF STUDY

This research mainly involves conducting experiment in laboratory. Scope of study in this research covers the drying process of coal samples at different temperature and stimulating the samples using sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3). The stimulation process will involve immersing the coal samples in different volume of acids to see the effect on coal porosity. This research also covers some part of sorption process of methane in coal sample to see the sorption capacity.

CHAPTER 2
LITERATURE REVIEW

2.1 COALBED METHANE

Coal is originated through the accumulation of vegetation that has undergone physical and chemical changes found in deposits called seams. Decaying of the vegetation, deposition and burying by sedimentation, compaction, and transformation of the plant remains into the organic rock found today are the changes it has undergone. Coals vary throughout the world in the types of plant materials deposited (type of coal), in the degree of metamorphism or coalification (rank of coal), and in the range of impurities included (grade of coal). (Miller, 2005)

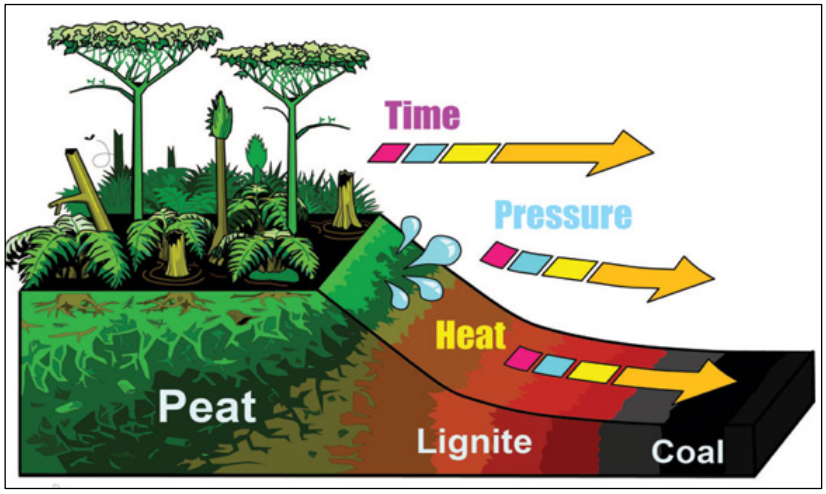


Figure 1 Formation of coal (Kentucky Geological Survey, 2012)

The rank of coal and an indication of the extent of metamorphism the coal has undergone are called the degree of coal maturation. Rank is also a measure of carbon content as the percentage of fixed carbon increases with extent of metamorphism. Lignites and subbituminous coals are referred low in coal rank, while bituminous coals and anthracites are classified as high-rank coals in the United States (Miller, 2005). The coal rank increases from lignite to anthracite in the process of

coalification (Bell et al., 2011).

Methane is primarily stored in coal through adsorption onto the coal surface; thus the maximum gas holding potential of a reservoir is determined by pore surface area (as opposed to pore volume in a conventional reservoir). Most methane adsorption occurs in micropores although macropores, mesopores, and micropores are present in the coal matrix. The methane molecule may actually stretch in many of the micropores, minutely, the pore and thus with de-gassing of the reservoir, could result in matrix shrinkage, allowing opening of the fracture (cleat) system in the coal and thus enhancing permeability. In determining porosity and permeability character, the organic composition of the coal is most important, and thus maximum gas holding capacity. In general, the higher the vitrinite (organic component of coal) content, the higher the gas holding potential (and ultimately the amount of desorbed gas) and permeability. (Moore, 2012)

Coalbeds are gas reservoirs that are naturally fractured, low pressure, and water saturated. The mechanism by which gas is stored and produced in coalbed reservoirs and sandstone reservoirs is quite different. Gas is stored in the pore space in a conventional sandstone reservoir, and flows through the pores into the fractures and the wellbore. In a coal seam reservoir, the majority of the gas is adsorbed on the surface of the coal matrix, while some free gas may exist in the coal deposits. The reservoir pressure must be reduced to produce this gas, so that it can be desorbed and released from the matrix into the fractures. The gas can then migrate through the fractures and coal cleat system and flow into the wellbore. (Amani & Juvkam-Wold, 1995)

In general, the gas is adsorbed to the coal matrix and is transported through the cleat system. At the top left of Figure 2, the relationship between face and butt cleats is shown in plan view of a coalbed, along with conventions used in classification of the cleat geometries. At the top right of Figure 2, cleat hierarchies are shown in cross-sectional view. The bottom picture in Figure 2, plan view combined with a cross-sectional view, showing relationships for the larger-scale cleat system. (Tonnsen & Miskimins, 2011)

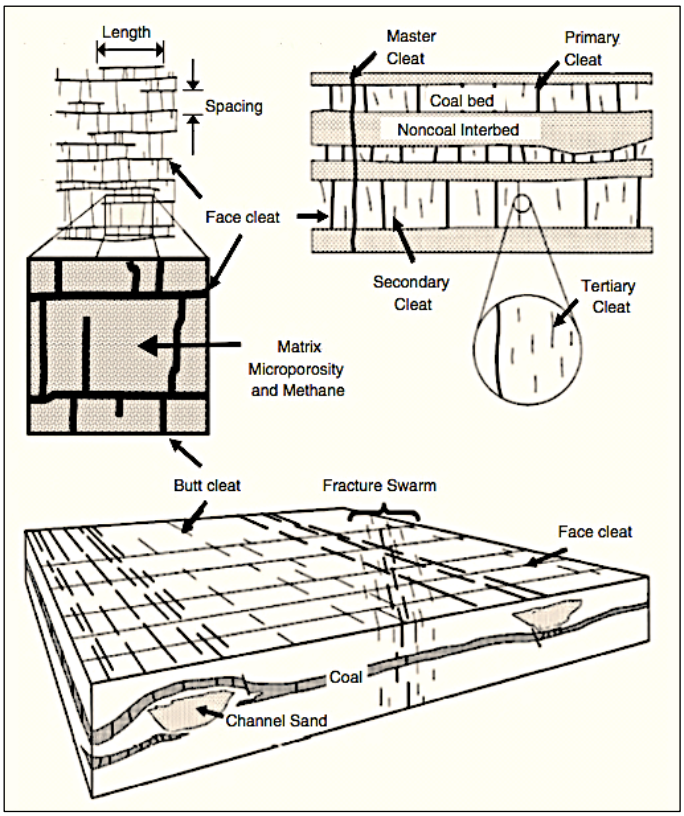


Figure 2 The relationship between the microporosity and macroporosity in a coal (Tonnsen &Miskimins, 2011)

Initially the natural fractures of the coal are typically water saturated. In order to achieve any significant gas production, this water has to be removed. Dewatering of the coal seam allows the gas to be desorbed from the coal matrix because it reduces the hydrostatic pressure of the reservoir. At the same time, reducing saturation level of the water in the reservoir increases the relative permeability of gas, thereby permitting the desorbed gas to flow to the wellbore. When the bottom hole pressure is minimized, the maximum gas production is achieved. (Amani & Juvkam-Wold, 1995)

The ability of water and gas to flow through coal deposits varies greatly, not only from basin to basin but within a given seam and over the course of depletion the ease with which a fluid moves through the interconnected pores and fissures of a rock is term permeability. Permeability of a coal deposit to gas and water depends on the interplay of these three influences; gas and water saturations, in-situ stresses, and sorbed gas content. (Seidle, 2011)

A function of the rock is the absolute permeability of a coal, not the fluids flowing

through it. Effective permeability of a fluid flowing through a coal depends on fluid properties and saturations as well as absolute coal permeability. Gas and water saturations in the cleats vary areally and over time as coal gas production usually involves dewatering of a coal seam. The mobility of both gas and water is affected by the interplay between them in the cleats, making gas-water relative permeabilities one of the controlling influences in coal gas production. Similar to conventional reservoirs, gas-water relative permeability behavior in coals is measured experimentally because it is difficult to predict. (Seidle, 2011)

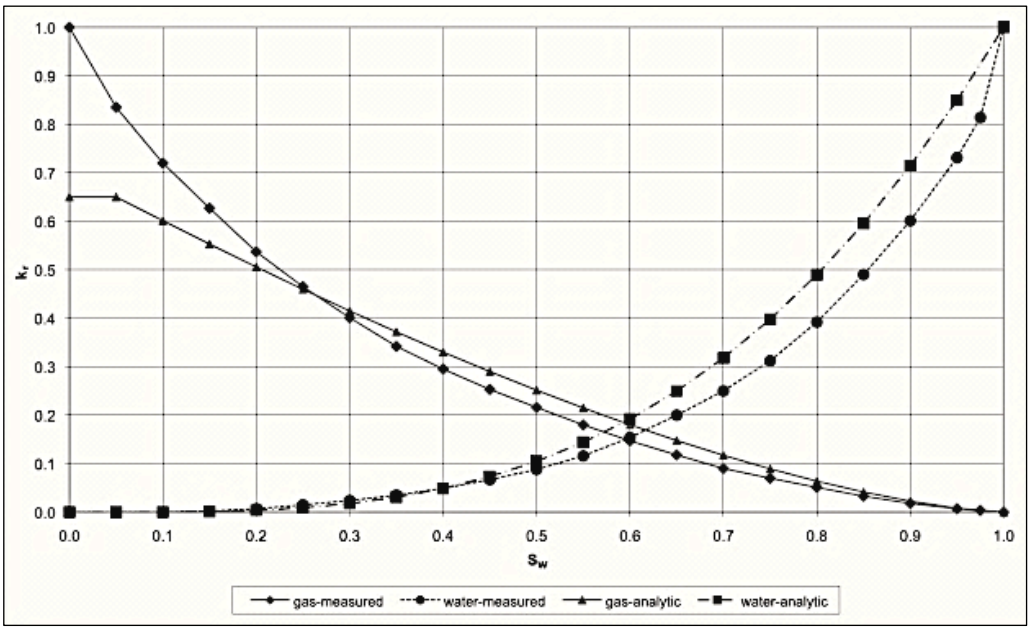


Figure 3 Measured and calculated gas-water relative permeabilities-San Juan coal (Seidle,2011)

2.2 ACTIVATED CARBON

The production of activated carbons involves two main steps that are the carbonization of the carbonaceous raw material at temperatures below 800 degree C in an inert atmosphere and the activation of the carbonized product. All carbonaceous materials can change their form into activated carbon, but the properties of the final product may not be the same. It depends on the nature of the raw material used, the nature of the activating agent and the condition of the activation process. (Bansal et al., 1988)

During the process of carbonization, nearly all of the non-carbon elements such as oxygen and hydrogen are removed as volatile gaseous products by the pyrolytic

decomposition of the starting material. The residual elementary carbon atoms group themselves into stacks of flat, aromatic sheets cross-linked in a random manner. These sheets are irregularly arranged, which leaves free interstices. These interstices give rise to pores, which makes activated carbons excellent adsorbents. (Bansal et al., 1998)

Tarry matter or the products of decomposition filled the pores during the carbonization process. These pores also at least blocked partially by the disorganized carbon. During the activation process, the pore structure in carbonized char is further generated and improved, which then introduced a form that contains the greatest possible number of randomly distributed pores of various sizes and shapes, from the carbonized raw material. The distributed pores giving rise to an extended and very high surface area of the product. (Bansal & Goyal, 2005)

Usually, the strong developed internal surface in activated carbons is characterized by a polydisperse porous structure. It consists of pores with different sizes and shape. There are several different methods used to determine the shape of the pores but the accurate information has been difficult to obtain on the actual shape of the pores. The size of pores in activated carbon is said to be from less than a nanometer to several thousand nanometers. Three types of pore and the diameter size are listed in Table 1. (Bansal & Goyal, 2005)

Table 1 Group of pores in activated carbon (Bansal & Goyal, 2005)

Type of pores	Size of pores (diameter)
Micropores	Less than 2 nm
Mesopores	Between 2 and 50nm
Macropores	Greater than 50nm

The micropores constitute a large surface area to about 95% of the total surface area of the activated carbon, while the mesopores contribute to about 5% of the surface area of the carbon. However, the macropores are not consider importance to the adsorption process in activated carbon because their contribution to surface area does not exceed 0.5 m^2/g. These macropores act as a channel for the adsorbate molecules to move into the micropores and mesopores. (Bansal & Goyal, 2005)

2.3 BREAKTHROUGH CURVE

The process in which one or more components from a gas stream are adsorbed on the surface of a solid is called gas adsorption. The differences in molecular weight, shape, or polarity can accomplished the separation process because these differences give rise to some molecules being held more strongly on the surface than others or because the pores are too small to admit the larger molecules. (Manual GACU)

Adsorbent is the solid that take up the gas, and the gas taken up on the adsorbent surface is adsorbate. Many adsorbents are highly porous materials, and adsorption takes place mainly on the walls of the pores or at specific sites inside the particle. The adsorbate (or the gas) is held strongly enough to allow complete removal of that component from the fluid with very little adsorption of other components in most applications. (Manual GACU)

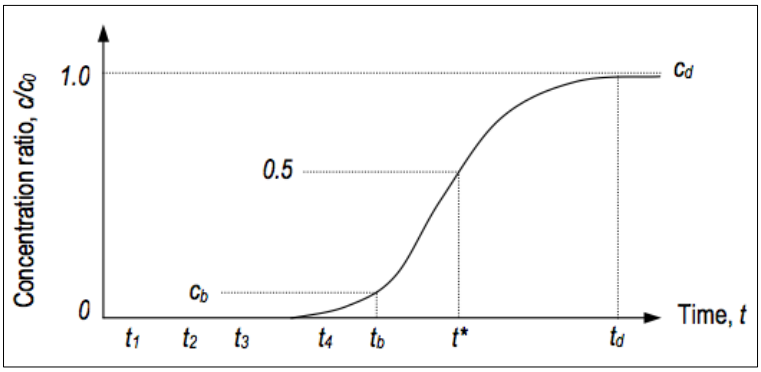


Figure 4 Breakthrough curve (Manual GACU)

Figure above shows the concentration curve of the fluid leaving the bed vs time. The curve is called breakthrough curve. As the fluid continues to flow, the S-shaped mass transfer region moves along the bed with time. The exit concentration is practically zero at t_1, t_2 and t_3. It remains zero until the mass transfer zone starts to reach the end of the bed at a time before t_4. The outlet concentration starts to rise until it reaches some limiting permissible value, or break point. The maximum allowable concentration of the outlet fluid represented by the break point concentration, c_b, and is often taken as a relative concentration, c/c_o of values 0.01 and 0.05. The relative concentration rises very rapidly until time t* after the break point is reached, then more slowly approaching c_d, which is the end of the breakthrough curve where the adsorption bed is considered ineffective. The value for c_d and feed concentration, c_o, is usually equal. (Manual GACU)

2.4 WELL STIMULATION

Even though the initial production rate of the gas can be very high in some wells, over time it decreases to a level where the production can be uneconomic.

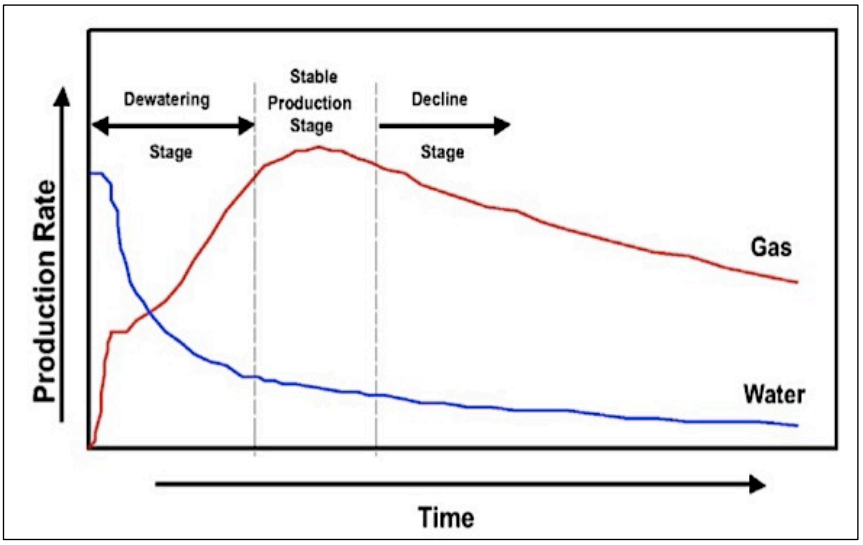


Figure 5 Water and gas production over time (U.S. EPA)

Figure above showing three stages of CBM production. The production increases exponentially during the dewatering stage and it reaches the maximum production in stable production stage. On the other hand, the gas production keeps decreasing during the decline stage. It shows that the production keeps decreasing over time.

Coalbed reservoir can be stimulated to increase the gas production. Stimulation is defined as a treatment performed to restore or enhance the productivity of a well. Two main groups of stimulation treatments are hydraulic fracturing treatments and acidizing treatments. Fracturing treatments are performed above the fracture pressure of the reservoir formation and create a highly conductive flow path between the reservoir and the wellbore. Acidizing are generally designed to restore the natural permeability of the reservoir and performed below the reservoir fracture pressure. (Oilfield Glossary)

Hydraulic fracturing is a technique to improve the production efficiency of oil and coalbed methane wells, used by the oil and gas industry. Hydraulically enlarging and/or creating fractures in the coal zones can enhance the extraction of coalbed methane. The resulting fracture system facilitates pumping of groundwater from the

coal zone, thereby reducing pressure and methane is able to be released from the coal and more easily pumped through the fracture system back to the well (and then through the well to the surface) (U.S. EPA). Acidizing is often used to remove near-wellbore damage and improve well productivity. Acidizing can be effective in sandstones where significant acid penetration is possible, but the depth of acid penetration in carbonates is often extremely limited because acid is consumed rapidly owing to the greater solubility of carbonates in acid (Xiong, 1994).

The most common form of completion/stimulation is hydraulic fracturing of coalbeds. It is not fundamentally different from fracturing of conventional formations, although some adaptions have certainly been made (Palmer, 1992). On the other hand, more study has to be made for better understanding of the processes occurring in coal for acidizing technique which is currently lacking in petroleum industry.

2.5 COAL REACTION WITH ACID

Acid is defined as a substance with particular chemical properties including turning litmus red, neutralizing alkalis, and dissolving some metals; typically, a corrosive or sour tasting liquid. Acids are compounds that release hydrogen ions (H+) when dissolved in water. Any solution with a pH of less than 7 is acidic, strong acids such as sulfuric or hydrochloric acid having a pH as low as 1 or 2. (Oxford Dictionaries)

A research has been made on reactions of a bituminous coal with sulfuric acid. Useful ion-exchange materials are produced when bituminous coals react with concentrated sulfuric acid. Oxidation and sulfonation involved in the reaction introduced carboxyl and sulfonic acid groups. Apart from that, the chemical changes that occur in the coal substance can also be noticed. (Kinney & Gray, 1959)

An examination on physical properties has been made. Large surface are is important for ion exchangers. The surface areas obtained under various conditions show that both temperature and time of reaction increase the area. (Kinney & Gray, 1959)

Table 2 Sulfonation data (Kinney & Gray, 1959)

	Temp. (^{0}C)	Time (days)	Surface area (m^2/g)
Raw coal (without react with acid)	-		2.7
Coal react with sulfuric acid	25	5	2.3
		10	0.002
		20	0.12
		31	1.5
	50	1	3.1
		3	16.0
		5	-
		8	54.0
	100	1	7.2
		2	101.0
		5	-
		8	222.0
	110	1	4.5
		3	158.0
		8	183.0
	150	1	178.0
		3	272.0

From Table 2, it shows that the original coal having a surface area of 2.7(m^2/g). At 25^{0}C, the surface areas are smaller than the original coal. This condition suggests that the reaction of the coal with acid is sealing off the coal pores. At higher temperature (50^{0}C, 100^{0}C, 110^{0}C and 150^{0}C), the surface areas are bigger than the original coal. This indicates that the dispersion has increased and new surface areas are developed. From the observation on the dispersion of sulfuric acid and the increment of surface area, a hypothesis is made which is, during the dispersion process, the acid molecules exert their way between the coal lamella. (Kinney & Gray, 1959)

Graphs below are plotted based on the results obtained from the research done by Kinney & Gray (1959).

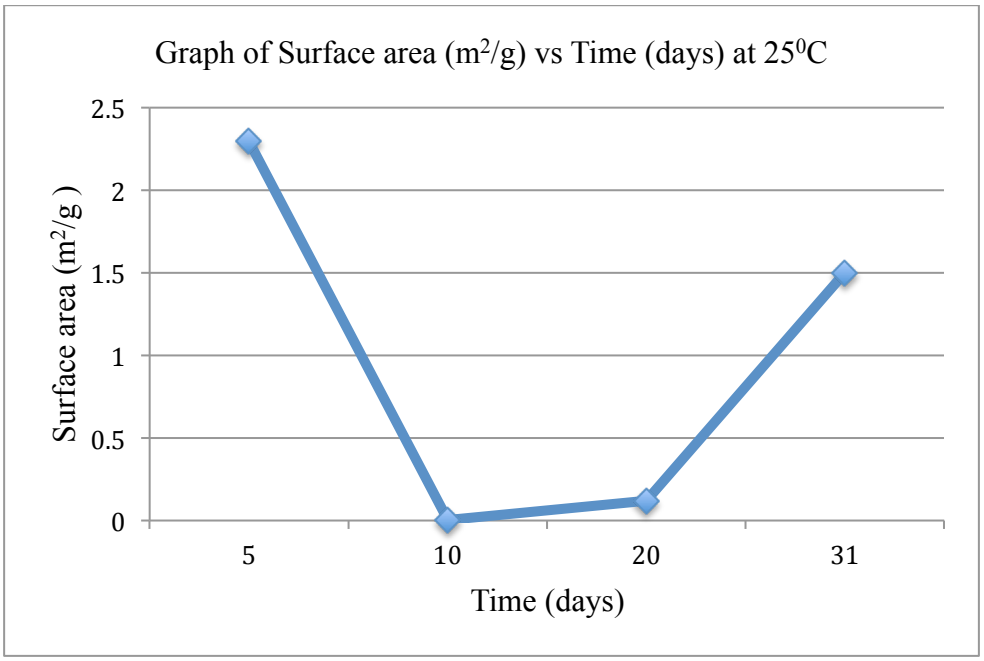


Figure 6 Co-relation between surface area and time at 25°C (Modified from Kinney & Gray, 1959)

At 25^{0}C, the surface areas noted at day 10 and day 20 are decreasing. There is no specific reason explained about this condition in the report but at this temperature, coal pores are being closed off due to the reaction of coal with the acid and the acid molecules are still not widely dispersed.

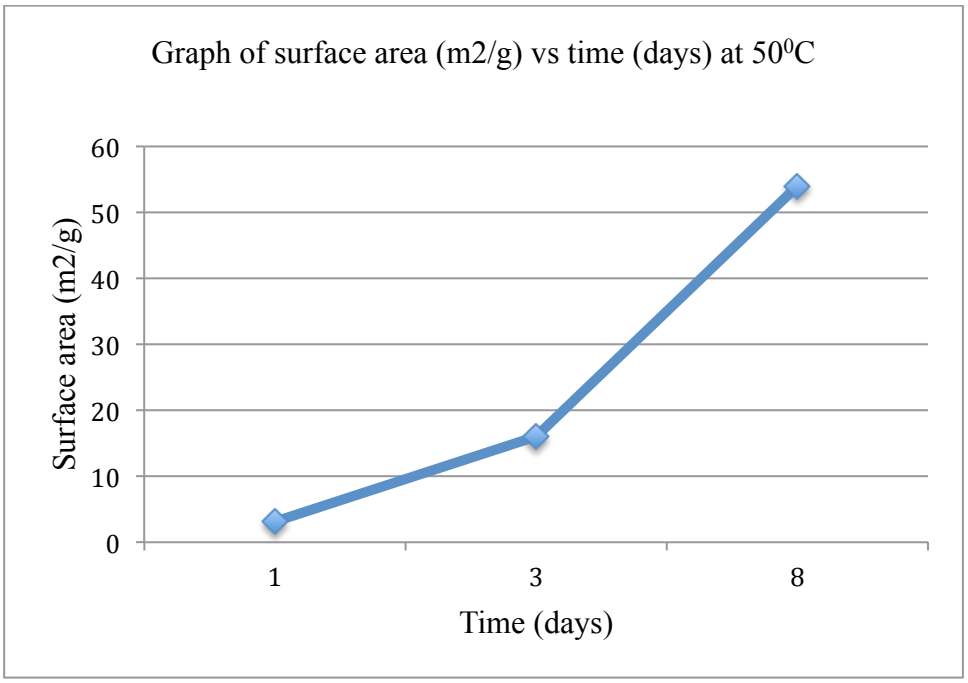


Figure 7 Co-relation between surface area and time at 50^{0}C (Modified from Kinney & Gray, 1959)

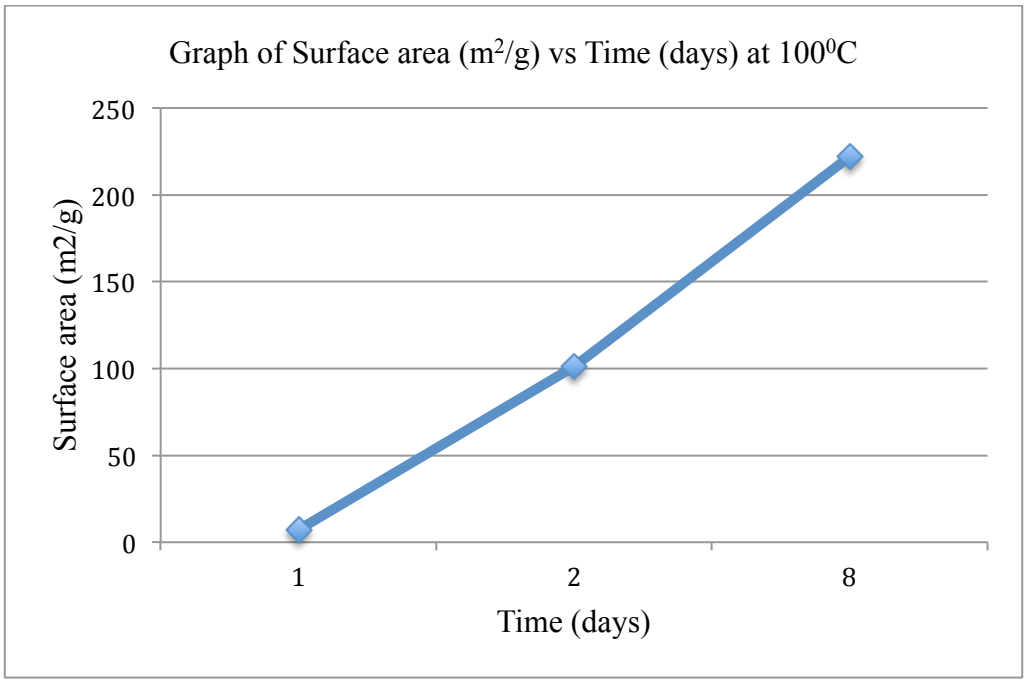


Figure 8 Co-relation between surface area and time at 100^{0}C (Modified from Kinney & Gray, 1959)

At 50^{0}C and 100^{0}C, there are no results on surface area being noted at day 5 but from the graphs plotted in Figure 7 and Figure 8, it shows that the surface areas are kept increasing. These new surface areas developed are due to the dispersion of acid molecules in the coal lamella.

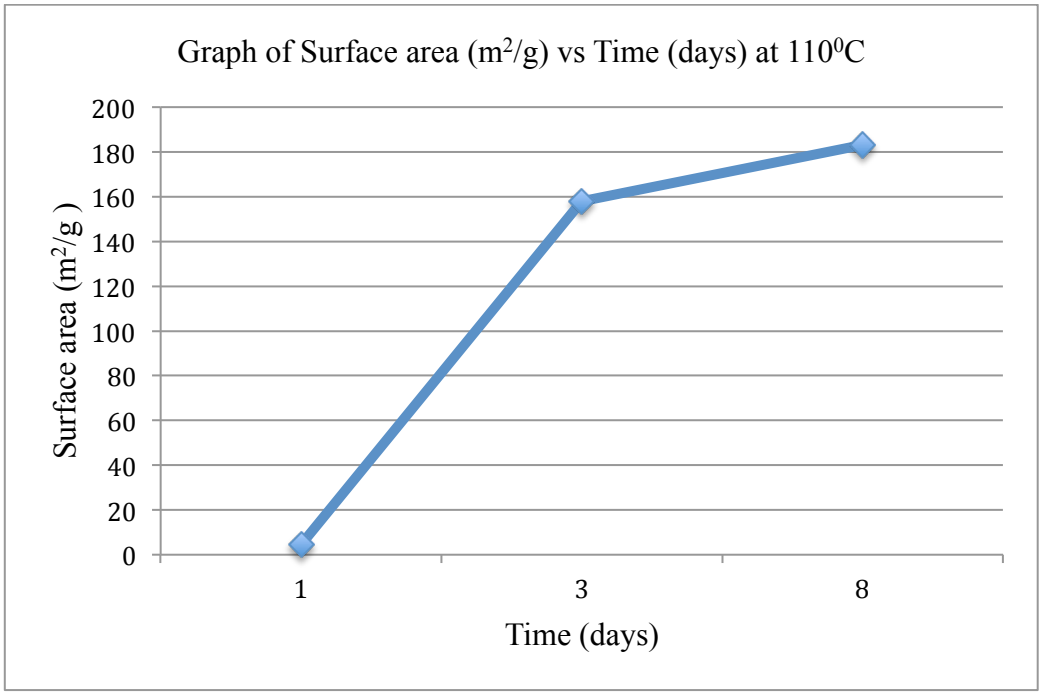


Figure 9 Co-relation between surface area and time at 110^{0}C (Modified from Kinney & Gray, 1959)

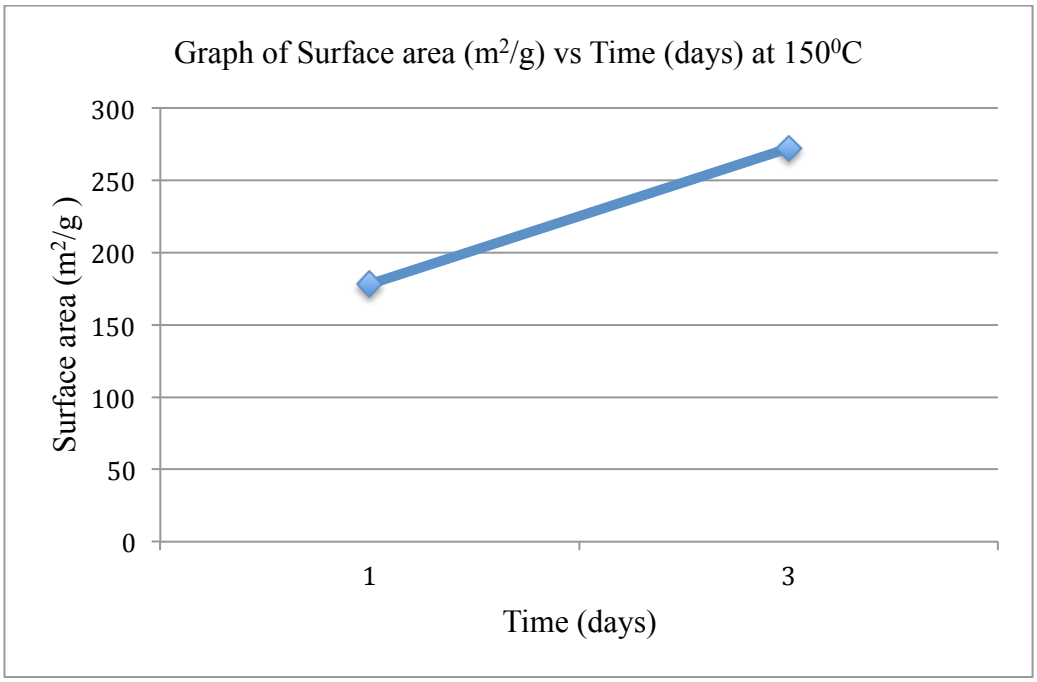


Figure 10 Co-relation between surface area and time at 150^{0}C (Modified from Kinney & Gray, 1959)

Besides at 50^{0}C and 100^{0}C, the new surface areas can also be developed at 110^{0}C and 150^{0}C. Based on the graph plotted in Figure 9 and Figure 10, it can be seen that the surface areas of the coal are increasing with increase in time of reaction. It can be conclude that, besides the time of reaction, the affect of temperature on the surface area can be noticed. Extending the duration of treatment at higher temperature can develop maximum surface area.

Another experiment has been found regarding adsorption from solutions of acetic acid on charcoal. The experiment that used 20g of active charcoal is done to meet the objective, which is to determine the K and N of the Freundlich adsorption isotherm (Juphil, 2009).

From the analysis made, dissolved substances from solution can be adsorbed by solid surfaces. Part of the acid is removed by the carbon when a solution of acetic acid in water is shaken with activated carbon, and the concentration of the solution is also decreased. There are some factors that the degree to which a solid will adsorb material, which are temperature, nature of molecule being adsorbed, degree of surface pore structure, and solute concentration and solvent. (Juphil, 2009)

It has been concluded that, adsorption from the solution obeys the general principle that laid down for the adsorption of gasses. Freundlich isotherm and Langmuir isotherm represent the variation of extend of adsorption with the concentration of solute. The molecules that have strong bond with the solid surface are the molecules that come into contact with it. The amount of acetic acid (adsorbate) adsorbed per gram of charcoal (adsorbent) depend on several factors such as surface area of the charcoal, the temperature of the solution and the adsorbate concentration in solution. (Juphil, 2009)

Another paper has been found regarding the mechanism of oxidation of low rank coal by nitric acid. The coal sample used is from the Fushun west opencast coal mine in China. Having carbon content of 74.43%, hydrogen content 5.26%, oxygen content 9.07% and nitrogen content 1.31%, the coal was piled up for long time and changed to weathered coal. According to the research done, the coal sample was crushed into particles, having the diameter of 0.15mm to 0.25mm. (Shi et al., 2012)

The coal samples were pretreated, for removing ash purposes, using hydrochloric acid and hydrofluoric acid. 8mol/L of nitric acid was mixed with the deashing coal particles after the pretreatment process, with the ratio of 1g to 2mL. After stirred for 3 minutes, the mixture was kept for oxidation for 48hours. Later on, using deionized water, the mixture was washed until the pH value for the washing liquid was higher than 5.5. The samples were dried at 60 ^{o}C until the weight remained constant after being filter using filter paper. (Shi et al., 2012)

Analysis made on the pore size and specific surface area measurement. From the result obtained, the de-ashing coal and nitric acid oxidized coal having the specific surface areas of 1.074 m^2/g and 1.634 m^2/g respectively, while the pore volumes were $9.936*10^{-3}$ m^2/g and $1.735*10^{-2}$ m^2/g. The average pore radius was 36.27nm for former and 42.00nm for latter. The paper concluded that, pore radius and pore volume of the de-ashing coal were increased due to nitric acid oxidation. (Shi et al., 2012)

CHAPTER 3
METHODOLOGY

Methodology in this project involves conducting experiment using special equipment in the laboratory and using chemicals to stimulate the samples. Three different acids are use to stimulate coal samples separately. The results from the experiments will then be recorded and analyzed.

3.1 PROJECT ACTIVITIES

Procedure in conducting an experiment is important to produce the desire results. To make sure the experiment is successfully done, the procedures need to be understand carefully to avoid any mistakes while conducting experiments thus avoiding any laboratory hazards.

Materials:

1. Malaysian sub-bituminous coals
2. Sulfuric acid, H_2SO_4 (wt. 95-97%)
3. Hydrochloric acid, HCl (wt. 37%)
4. Nitric acid, HNO_3 (wt. 69-70%)

ECONOMIC STUDY

An analysis is made on the price of acids. A price comparison between different acids is made before choosing the acids to be used in the experiment. Lower price acid is more recommendable to be used. Besides price, the availability of the acids in the laboratory is also being considered. Since three types of acids are going to be used in the experiment, the acids chosen are hydrochloric acid, sulfuric acid and nitric acid. The price of available acids is listed in Table 3.

Table 3 List of acid prices (Chemical Laboratory, UTP)

No	Item Name	Unit of Measure	Estimated Price (RM)	Price produce by companies (RM)						
				Teknologi Foram	Adlizz	Premier Enterprise	Zastra	Benua Sains	Bibi Scientific	Kinetic Chemicals
1	Hydrochloric Acid	2.5 litre/bottle	75.00	52.00	-	82.20	43.00	60.00	67.00	86.00
2	Nitric Acid	2.5 litre/bottle	80.00	78.00	120.00	97.90	-	138.00	94.00	115.00
3	Phosphoric Acid	2.5 litre/bottle	145.00	145.00	-	176.90	93.00	120.00	170.00	169.00
4	Sulfuric Acid	2.5 litre/bottle	75.00	70.00	-	82.20	46.00	70.00	-	90.00

	Cheapest price and available

3.1.2 Experiment 1: Sorption Process using GACU

Procedure:

1. Put fresh coal sample (without acid) inside Gas Adsorption Column Unit (GACU) for sorption process.
2. Record the percentage composition of gas that can be sorbed by coal sample and the outlet flow rate of the gas.
3. Inject 1.0ml of sulfuric acid in the same coal sample and leave it for two days at constant temperature.
4. Put the sample inside Gas Adsorption Column Unit (GACU) for sorption process.
5. Record the percentage composition of gas that can be sorbed by coal sample and the outlet flow rate of the gas.
6. Repeat Step 3 by injecting 1.5ml of sulfuric acid in the same coal sample.
7. Repeat Step 4 and record the percentage composition of gas that can be sorbed by coal sample and the outlet flow rate of the gas.
8. Inject 1.0ml of hydrochloric acid in other coal sample (same rank of coal) and leave it for two days at constant temperature.
9. Repeat Step 4 and record the percentage composition of gas that can be sorbed by coal sample and the outlet flow rate of the gas.
10. Repeat Step 8 by injecting 1.5ml of hydrochloric acid in the same coal sample.
11. Repeat Step 4 and record the percentage composition of gas that can be sorbed by coal sample and the outlet flow rate of the gas.
12. Inject 1.0ml of nitric acid in other coal sample (same rank of coal) and leave it for two days at constant temperature.
13. Repeat Step 4 and record the percentage composition of gas that can be sorbed by coal sample and the outlet flow rate of the gas.
14. Repeat Step 12 by injecting 1.5ml of nitric acid in the same coal sample.
15. Repeat Step 4 and record the percentage composition of gas that can be sorbed by coal sample and the outlet flow rate of the gas.

Objective of GACU

Gas Adsorption Column Unit is use to study the adsorption and desorption of gases using adsorbents.

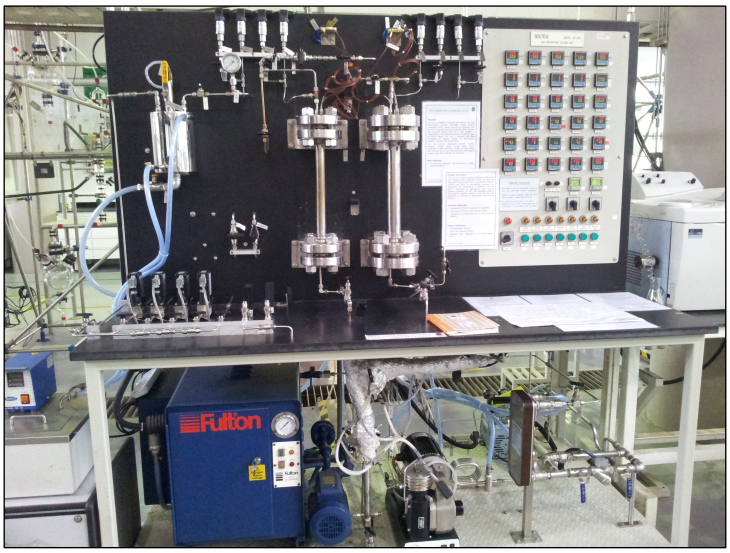


Figure 11 Gas Adsorption Column Unit (Available in block 3, UTP)

Principle of GACU

The unit is capable to separate hydrocarbon and non-hydrocarbon mixture, especially volatile organic chemicals (VOC), natural gas and its impurities, with the aid of adsorbent (such as molecular sieve, zeolites and activated carbon). The unit is also capable of regeneration of the adsorbent using hot purge N_2 gas, air and/or steam. The unit is equipped with data acquisition and logging systems for temperature, pressure, flow rate and concentration. (Chemical Laboratory, UTP)

The unit includes adsorption columns, heating sleeves, syringe pump, in-line static mixer, compressor, steam generator, heater, air dryer, water trap, vacuum pump, gas chromatograph, data logging system, mass flow controller and flow meter. (Chemical Laboratory, UTP)

3.1.2 Experiment 2: Porosity Measurements

Procedure:

1. Measure the weight of each coal sample.
2. Put the samples in the oven for 2 hours at 100℃ for drying purposes.
3. Immediately record the weight of each coal sample.
4. Immerse each sample in 5ml, 10ml, 15ml, 20ml, and 25ml of sulfuric acid, hydrochloric acid and nitric acid separately for 6 hours at constant temperature.
5. Separate each sample from the acid by filtering the sample using filter paper.
6. Record the weight of each coal sample.
7. Repeat Step 1 using other coal samples (same rank of coal).
8. Repeat Step 2 by changing the oven temperature to 50℃.
9. Immediately record the weight of each coal sample.
10. Repeat Step 4 and Step 5.
11. Record the weight of each coal sample.

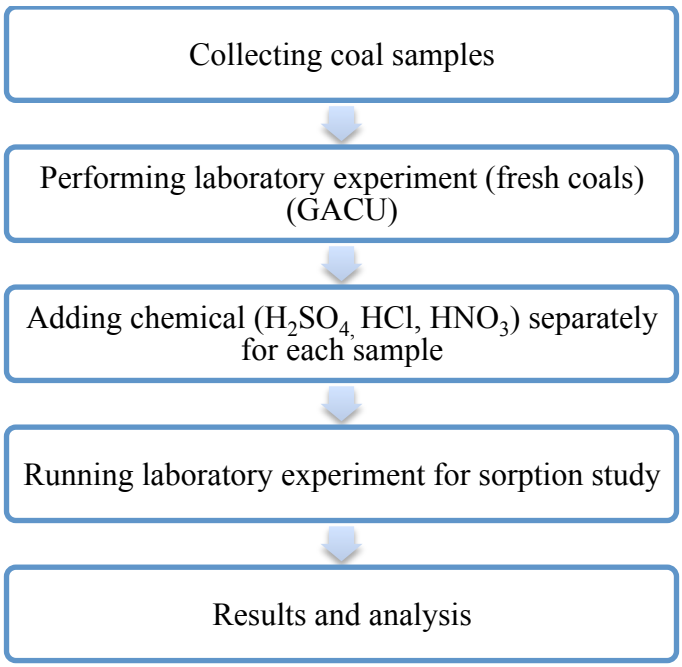
3.2 TOOLS REQUIRED

Tools required while conducting the experiments are:

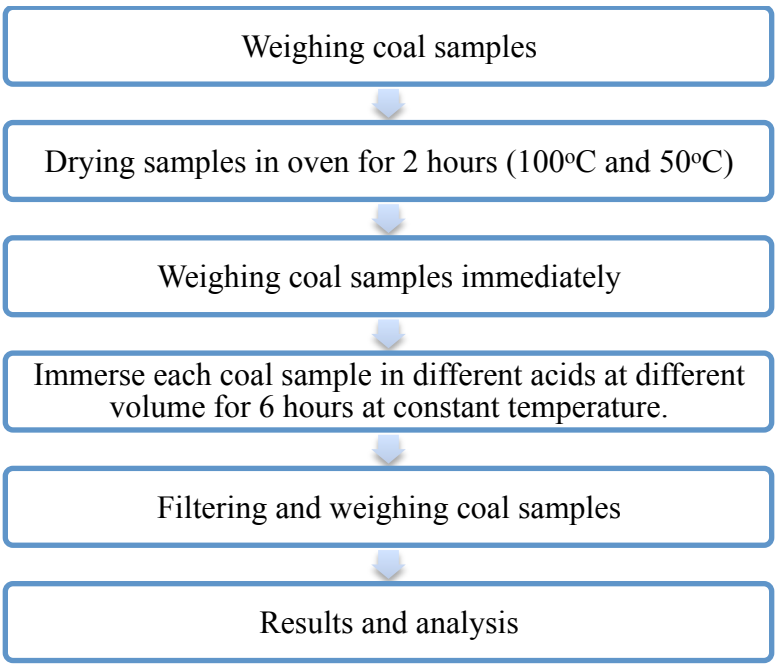
1. Weighing scale
2. Gas Adsorption Column Unit (GACU)
3. Oven
4. Syringe
5. Filter paper

3.3 RESEARCH METHODOLOGY

3.3.1 Experiment 1: Sorption Process using GACU



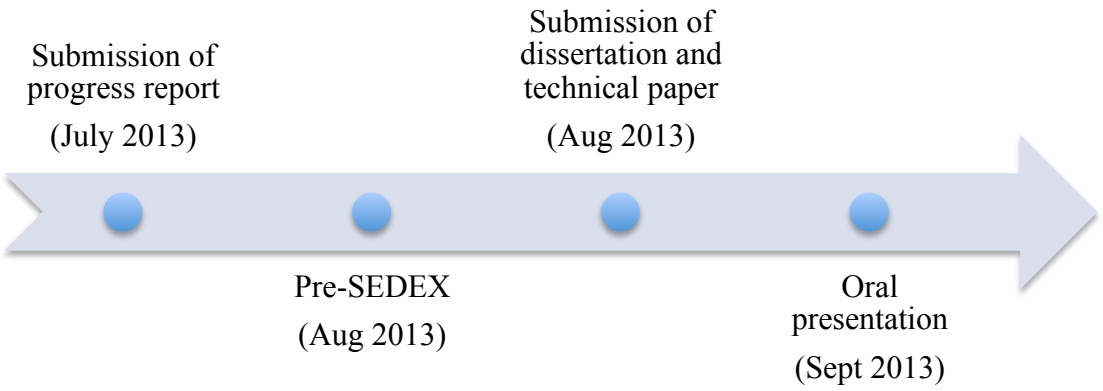
3.3.2 Experiment 2: Porosity Measurements (Iqbal et al., 2013)



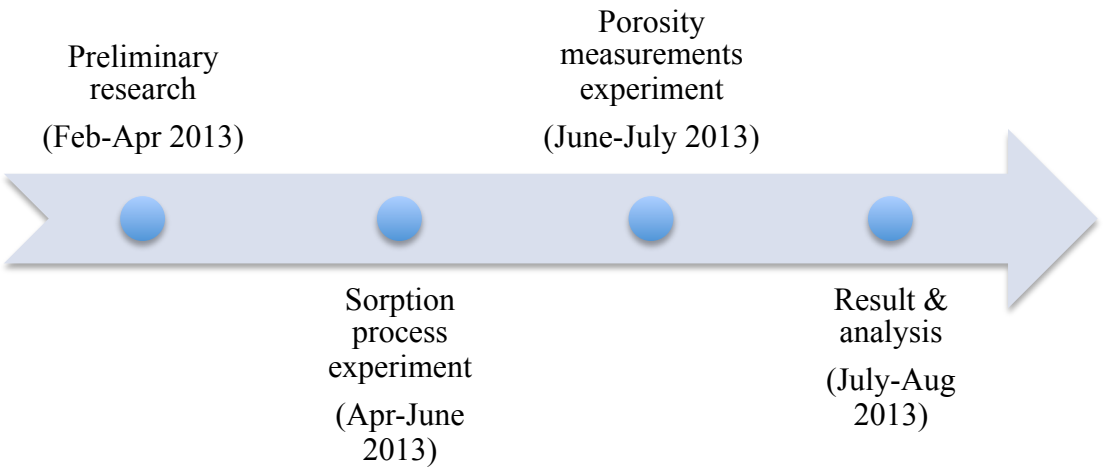
3.4 KEY MILESTONE

3.4.1 Final Year Project 1

3.4.2 Final Year Project 2



3.4.3 Experiments Key Milestone



3.5 GANTT CHART

3.5.1 Final Year Project 1

No	Detail/Week	1	2	3	4	5	6	7	Mid semester break	8	9	10	11	12	13	14
1	Selection of project topic															
2	Preliminary research work															
3	Submission of extended proposal defence															
4	Proposal defence															
5	Project work continues															
6	Submission of interim draft report															
7	Submission of interim report															

	Process
	Suggested milestone

3.5.2 Final Year Project 2

No	Detail/Week	1	2	3	4	5	6	7	Mid semester break	8	9	10	11	12	13	14
1	Project work continues															
2	Submission of progress report															
3	Project work continues															
4	Pre-SEDEX															
5	Submission of draft report															
6	Submission of dissertation (soft bound)															
7	Submission of technical paper															
8	Oral presentation															
9	Submission of project dissertation (hard bound)															

	Process
	Suggested milestone

CHAPTER 4
RESULTS AND DISCUSSION

Information on the Malaysian coal samples used for the experiments is as below.

Source:	Mukah, Sarawak
Coordinate:	N5312734/E2293035
Coal rank:	Sub-bituminous
Moisture content:	20%
Volatile matter:	36%
Fixed carbon:	40%

4.1 EXPERIMENT 1: SORPTION PROCESS USING GACU

The experiment was started by crushing coal samples since the column can only be filled with granular size samples. After done weighing, the samples were poured inside the column. The process of assemble and dissemble of the column took about 45 minutes.

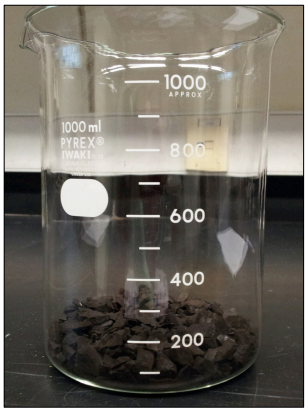


Figure 12 Crushed coal sample

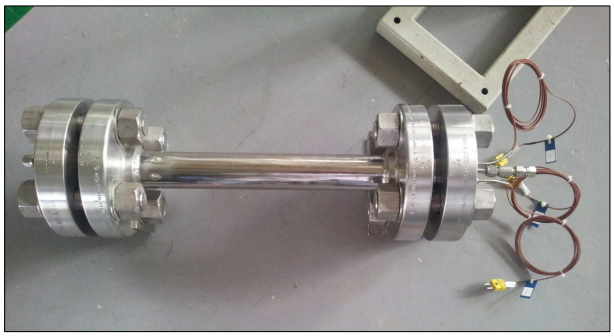


Figure 13 Column that needs to be assembled and dissembled

Leak test was done to make sure the column fitted correctly to the Gas Adsorption Column Unit (GACU). If bubbles appear, it means that there is leakage, and the column needs to be assembled and dissembled again.

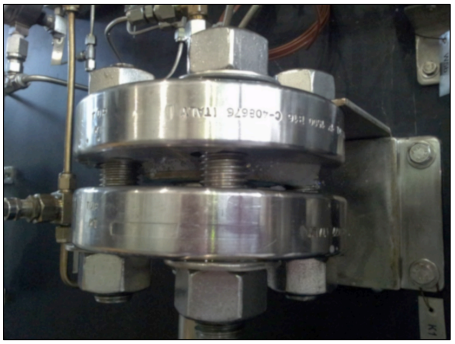


Figure 14 Bubbles appeared showing there is leakage

The experiment was started by switched on the vacuum pump to clear the impurities or any gasses left inside the column. This process took 30 minutes. Then, the experiment was carried on with few runs. Each run took 1.7 minute. After 1.7 minute, the second run was automatically started for another 1.7 minute, followed by the next run. After each 1.7 minute, the reading of the flow rate was recorded in Table 4. The runs stopped until a constant flow rate was obtained.

For every run, methane gas and carbon dioxide were passed through the column. Both gases having the same flow rate at inlet. The outlet, which was attached to the gas chromatograph, gave the result based on the percentage of gases released. Based from the outlet result, the percentage of gases adsorbed by the sample can be determined. In addition, when the recorded outlet flow rate reached a constant value, it indicated that the adsorption of gases by the coal sample was considered ineffective and has reached the adsorption limit.

Coal Sample without Acid

Weight: 70g

The result for percentage of gases at outlet and the outlet flow rate was recorded in the table below. The result shown in the table is the experiment done on fresh coal sample without injecting any acids.

Table 4 Result for coal sample without acid

Run	Time for each run (min)	Time accumulated (min)	Outlet Composition of CH_4 (%)	Outlet Composition of CO_2 (%)	Flow rate (litre/min)
1	1.7	1.7	Blank test		
2	1.7	3.4	68.2390	31.7610	1.49
3	1.7	5.1	67.9408	32.0592	2.09
4	1.7	6.8	67.8287	32.1713	2.09
5	1.7	8.5	67.9703	32.0297	2.09
6	1.7	10.2	67.8738	32.1252	2.09

From the results of outlet percentage for both gases in Table 4, the adsorption percentage can be calculated as below.

Adsorption percentage of CH_4 = 100% - Outlet composition of CH_4 (%)
Adsorption percentage of CO_2 = 100% - Outlet composition of CO_2 (%)

The adsorption percentage result is tabulated in Table 5.

Table 5 Adsorption result for coal sample without acid

Run	Time for each run (min)	Time accumulated (min)	Adsorption of CH_4 (%)	Adsorption of CO_2 (%)	Flow rate (litre/min)
1	1.7	1.7	Blank test		
2	1.7	3.4	31.7610	68.2390	1.49
3	1.7	5.1	32.0592	67.9408	2.09
4	1.7	6.8	32.1713	67.8287	2.09
5	1.7	8.5	32.0297	67.9703	2.09
6	1.7	10.2	32.1252	67.8738	2.09

Run 1 is for the blank test, which was run while closing the inlet of both gases. The importance of the blank test is to make sure that there is no impurities or any gas left inside the column. In simple words, to make sure the column filled with coal sample was clean from any impurities. It is necessary step to be done before started opening

the inlet to flow both gases through the column. For blank test, there must be no percentage composition for both gasses to confirm that the column was clean. If any values existed, the vacuum process has to be repeated until no percentage composition recorded.

After the blank test, the inlet for both gases was opened to flow the gases through the column. At Run 2, the coal sample has adsorbed more carbon dioxide, which was 68.2390% and lesser amount of methane gas, which was 31.7610%.

At Run 3, the adsorption percentage of methane gas increased to 32.0592% while for carbon dioxide, decreased to 67.9408%, which still showing that the coal sample was able to adsorb higher amount of carbon dioxide compared to methane gas.

At Run 4, the coal sample adsorbed a bit higher amount of methane gas, which was 32.1713% and the adsorption percentage for carbon dioxide was 67.8287%. From Run 2 to Run 4, it can be seen that the adsorption of methane gas kept increasing while for carbon dioxide, it kept decreasing. This suggests that, methane gas is strongly adsorbed by the coal at early stage of time.

Whereas At Run 5, the adsorption percentage of methane gas was decreased to 32.0297% while the adsorption percentage of carbon dioxide was increased to 67.9703%. This may be due to the gasses remained inside the column from the run before, thus the outlet gases that reached gas chromatograph affected the result.

Lastly, at Run 6, the adsorption percentage of methane gas was increased again to 32.1252% while decreased to 67.8738% for carbon dioxide, but it still showing that coal sample was able to adsorb more carbon dioxide compared to methane gas.

From these results, it can be concluded that the coal sample adsorbed higher amount of carbon dioxide and less amount of methane gas. The results for this experiment complies with the results by Yang and Zoback (2011), which stated that the adsorption capacity for carbon dioxide is larger compared to methane gas. However, different from Yang and Zoback (2011), which showed that the adsorption capacity for carbon dioxide is larger by approximately 4-5 times compared to methane gas,

the adsorption capacity for carbon dioxide in this experiment is only approximately 2 times compared to methane gas. This suggests that, carbon dioxide is weakly adsorbed to the coal surface.

Besides analyzing the percentage of outlet composition for both gases, the flow rate was used to analyze the adsorption capacity of the coal sample. A graph of Flow rate vs Time was plotted in Figure 15.

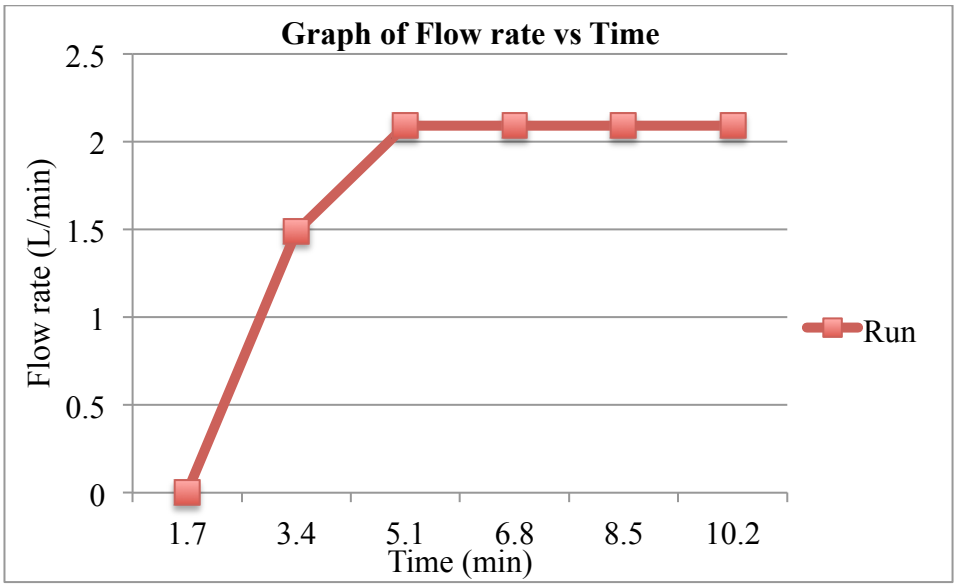


Figure 15 Graph of flow rate vs time

Figure above shows the graph of flow rate (L/min) vs time (min). The flow rates were recorded after 1.7 minute for every run until it became constant. The readings of flow rate were obtained from the equipment itself.

At Run 1, there was no flow rate reading because it was the blank test, which the inlet valve was closed to clean up the column. At Run 2, the first flow rate was obtained because the inlet valve was already opened. The flow rate was 1.49 L/min. It increased until Run 3, which was until 5.1 minutes. After 5.1 minutes, the flow rate started to became constant until 10.2 minutes, which was until Run 6. The constant flow rate was 2.09 L/min.

The constant flow rate shows that the coal sample has reached its maximum adsorption capacity. This is because at Run 3, when the flow rate started to become

constant, it means that the coal sample has fully adsorbed the gasses. It has reached its limit to adsorb more gasses, and after 5.1 minutes the adsorption was considered ineffective.

This was proved by the results of adsorption percentage in Table 5. At run 3, where the coal sample has reached its maximum adsorption capacity, the adsorption percentage for both gases also started became constant. It can be seen that from Run 3 until Run 6, the coal sample has adsorbed constant amount of methane gas, which was approximately 32.1%, and constant amount of carbon dioxide, which was approximately 67.9%.

The amount of both gases that can be adsorbed by the sample can only be determined by percentage value because the equipment does not produce result for specific amount of gases. Based on the literature review, the desorption of methane gas was predicted to be the same as what was adsorbed. As at Run 3, the coal sample has adsorbed approximately 32.1% of methane gas, meaning that it will desorb almost the same value of that gas.

Due to the unforeseen circumstances, the equipment broke down and the experiment cannot be continued to run coal samples that has been injected with acid. Based on the study that has been made, the time taken for the coal samples that has been injected with acid to reach its maximum adsorption capacity is expected to be faster due to the alteration of coal matrix by the acids.

5.2 EXPERIMENT 2: POROSITY MEASUREMENTS

After crushing and weighing, small size coals were collected as the coal samples.

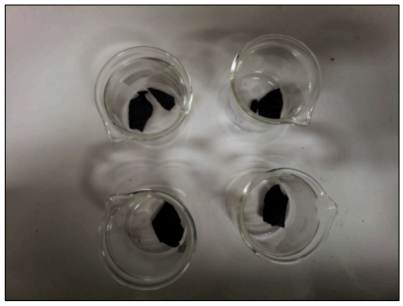


Figure 16 Preparation of coal samples

After done preparing, all samples were put in the oven for 2 hours for drying purposes. The temperature of the oven was set to be 100^0C. The weight for each sample was immediately recorded after the samples were taken out from the oven.

Then, each coal sample was immersed in 5ml, 10ml, 15ml, 20ml, and 25ml of hydrochloric acid, sulfuric acid and nitric acid separately. The coal samples were left in the acids for 6 hours at constant temperature (23^0C) for stimulation purposes.

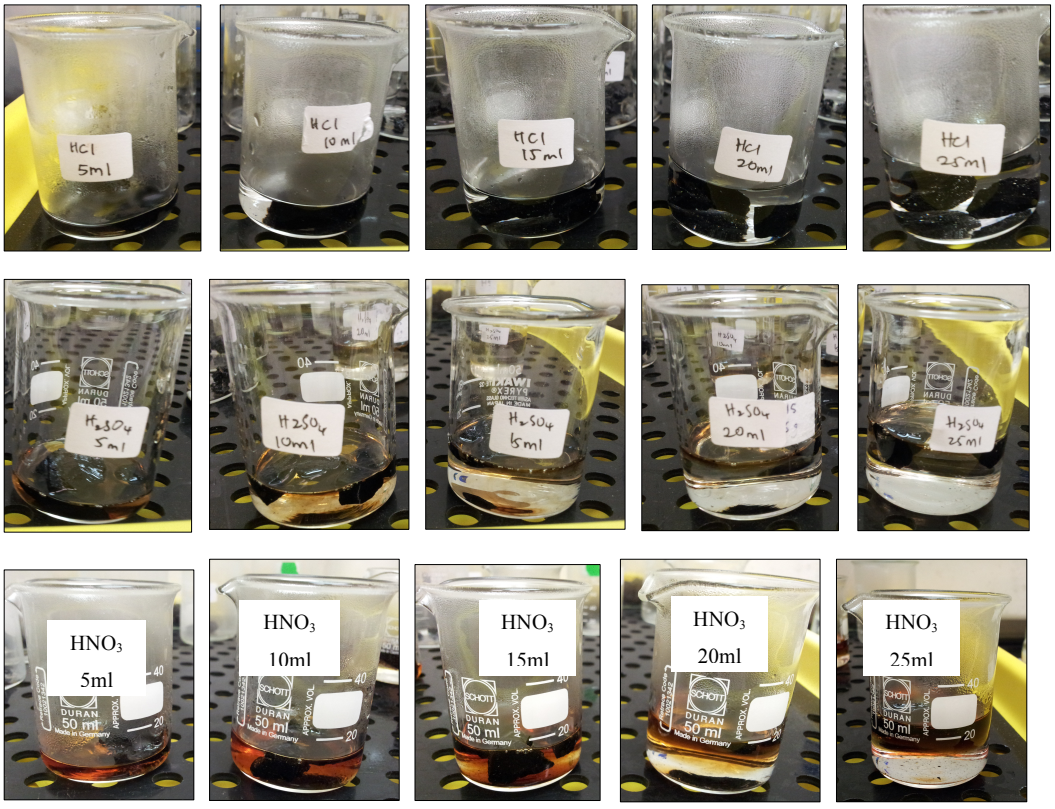


Figure 17 Samples immersed in different acids at different volumes and constant temperature of 23^0C

All acids used in this experiment were pure acids;

- Hydrochloric acid (wt. 37%)
- Sulfuric acid (wt. 95-97%)
- Nitric acid (wt. 69-70%)

After 6 hours, each sample was taken out and filtered using filter paper to separate the sample with acid. Then, the weight of each sample was measured again and recorded.

The procedures were repeated using coal samples with same rank, but the oven temperature was set to be 50^0C for drying purposes.

From the recorded data, calculation can be made based on formula to get the percentage of porosity.

Formula (Iqbal et al., 2013):

$$Porosity\ (\%) = \frac{\rho_{Mdry}\,(M_{wet} - M_{dry})}{\rho_{Mdry}\,(M_{wet} - M_{dry}) + \rho_w \times M_{dry}} \times 100\%$$

Where:

M_{dry} = Weight of coal after dry in oven, g

M_{wet} = Weight of coal after take out from acid, g

ρ_{Mdry} = Density of coal, 1.26 g/cm^3

ρ_w = Density of liquid (acid), g/cm^3

- Hydrochloric acid = 1.19 g/cm^3 (Merck SDS)
- Sulfuric acid = 1.84 g/cm^3 (Merck SDS)
- Nitric acid = 1.42 g/cm^3 (Fisher Scientific SDS)

Due to the brittle characteristic of coal, it was very hard to make the weight of each coal sample constant, but the samples were prepared to be in the range of 2.50g and 2.55g. The results are tabulated as in Table 6 and Table 7.

Table 6 Result for samples dry at 100^0C

Sample	Weight before dry in oven (g)	Weight after dry in oven (g)	Type of acid	Volume of acid (ml)	Weight after take out from acid (g)	Porosity (%)
1	2.5	2.10	HCl	5	2.63	21.09
2	2.5	2.07	HCl	10	2.65	22.88
3	2.5	1.88	HCl	15	2.51	26.19
4	2.52	1.87	HCl	20	2.56	24.67
5	2.5	1.90	HCl	25	2.66	29.75
6	2.52	1.89	H_2SO_4	5	3.51	43.2
7	2.5	2.15	H_2SO_4	10	5.30	50.08
8	2.5	1.84	H_2SO_4	15	4.91	53.33
9	2.5	1.93	H_2SO_4	20	5.31	54.53
10	2.5	1.90	H_2SO_4	25	5.47	56.27
11	2.51	1.89	HNO_3	5	3.05	35.26
12	2.51	1.9	HNO_3	10	3.31	39.7
13	2.51	1.87	HNO_3	15	4.41	54.65
14	2.51	1.8	HNO_3	20	4.48	56.92
15	2.52	1.8	HNO_3	25	4.87	60.21

Table 7 Result for samples dry at 50^0C

Sample	Weight before dry in oven (g)	Weight after dry in oven (g)	Type of acid	Volume of acid (ml)	Weight after take out from acid (g)	Porosity (%)
16	2.51	2.34	HCl	5	2.73	15
17	2.51	2.38	HCl	10	2.80	15.74
18	2.51	2.38	HCl	15	2.73	13.47
19	2.52	2.36	HCl	20	2.76	13.07
20	2.51	2.41	HCl	25	2.80	14.63
21	2.52	2.34	H_2SO_4	5	3.82	30.22
22	2.52	2.32	H_2SO_4	10	5.95	51.72
23	2.52	2.37	H_2SO_4	15	6.47	54.23
24	2.53	2.15	H_2SO_4	20	5.96	54.82
25	2.53	2.34	H_2SO_4	25	5.93	51.23
26	2.5	2.18	HNO_3	5	3.28	30.93
27	2.51	2.24	HNO_3	10	3.39	31.3
28	2.51	2.20	HNO_3	15	3.54	35.08
29	2.52	2.17	HNO_3	20	3.04	26.24
30	2.52	2.15	HNO_3	25	3.96	42.76

Below is the example of the calculation:

Sample 1 (using hydrochloric acid)

$$Porosity\ (\%) = \frac{1.26\ (2.63 - 2.10)}{1.26\ (2.63 - 2.10) + \ 1.19 \times 2.10} \times 100\%$$

$$= 21.09\%$$

Sample 6 (using sulfuric acid)

$$Porosity\ (\%) = \frac{1.26\ (3.51 - 1.89)}{1.26\ (3.51 - 1.89) + \ 1.84 \times 1.89} \times 100\%$$

$$= 43.2\%$$

Sample 11 (using nitric acid)

$$Porosity\ (\%) = \frac{1.26\ (3.05 - 1.89)}{1.26\ (3.05 - 1.89) + \ 1.42 \times 1.89} \times 100\%$$

$$= 35.26\%$$

From the results in Table 6 and Table 7, the graphs of Weight after take out from acid vs Volume of acid for samples dry at 100^0C and 50^0C were plotted.

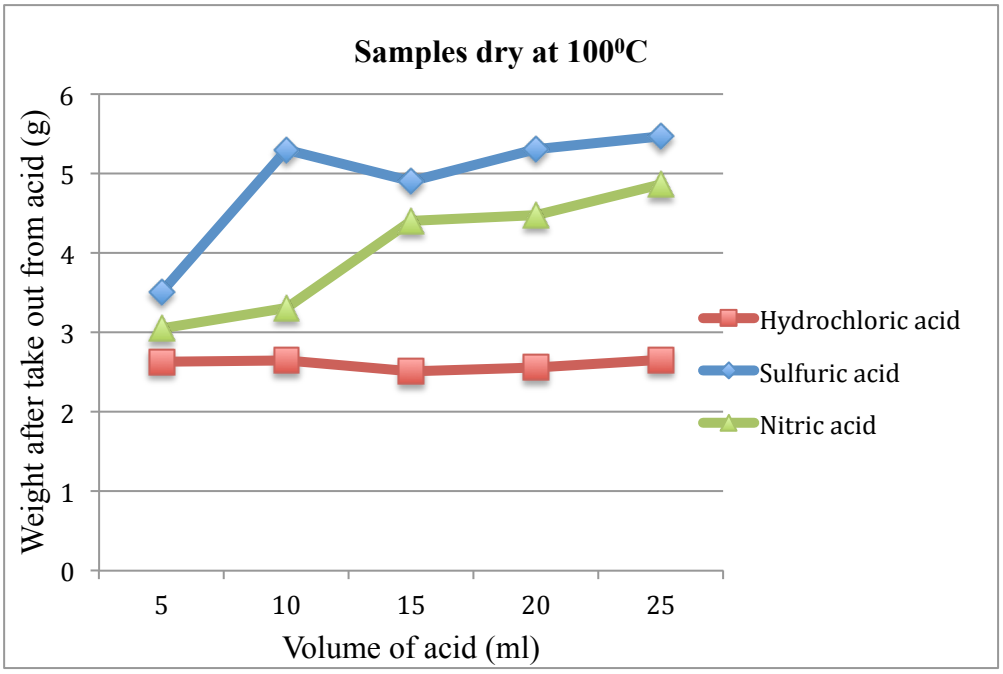


Figure 18 Graph of weight of coal after take out from acid vs volume of acid (at 100^0C)

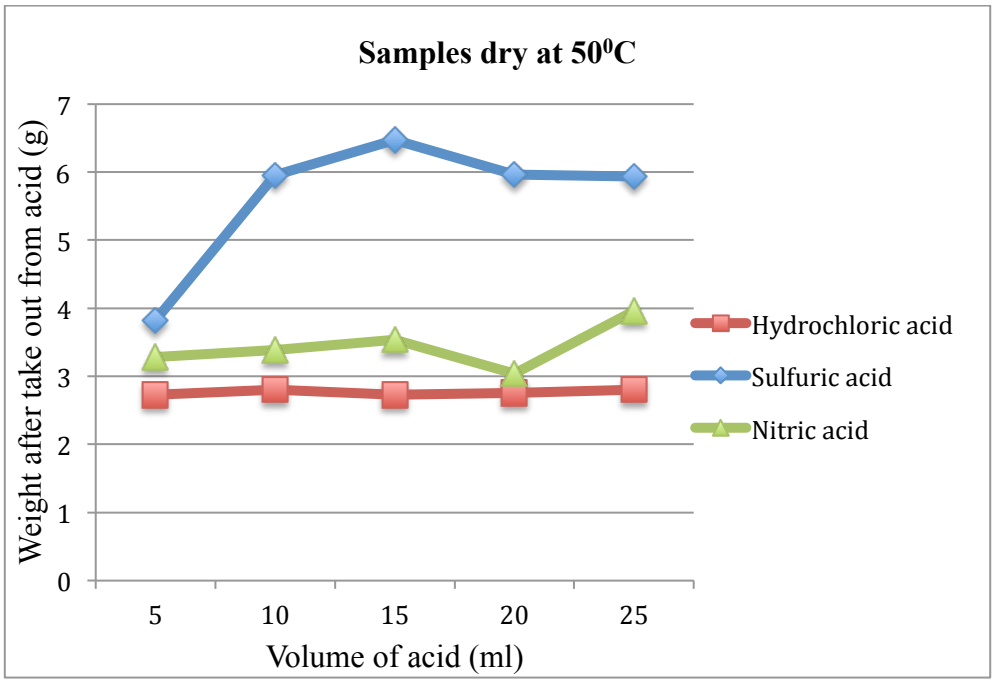


Figure 19 Graph of weight of coal after take out from acid vs volume of acid (at 50^{0}C)

From Table 6 and Table 7, the results showing that the weight after drying of coal sample has increase and decrease unevenly. This is due to the uneven shape of crushed sample. Eventhough the samples might be having the same weight before drying in oven, smaller size samples were dried easily compared to bigger size sample, thus the weight of smaller samples after dried in oven may be lower than bigger sample. The uneven decreased and increased of weight of coal samples after take out from acid may also due to this reason.

Graphs in Figure 18 and Figure 19 show that sulfuric acid gives better adsorption than hydrochloric acid and nitric acid. This is because, weight of the samples take out from sulfuric acids are heavier compared to weight of the samples take out from hydrochloric acid and nitric acid. It means that coal samples that have been stimulated by sulfuric acid have better adsorption compared to coal samples that have been stimulated by hydrochloric acid and nitric acid.

From the results obtained, comparison was being made between these three acids. Sulfuric acid has highest adsorption by the samples, followed by nitric acid and hydrochloric acid. In addition, higher volume of acid, result in better adsorption

since the coal samples were increased in term of weight after being immersed in different volumes of acid.

From the results in Table 6 and Table 7, the graphs of Porosity vs Volume of acid for samples dry at 100^0C and 50^0C were plotted.

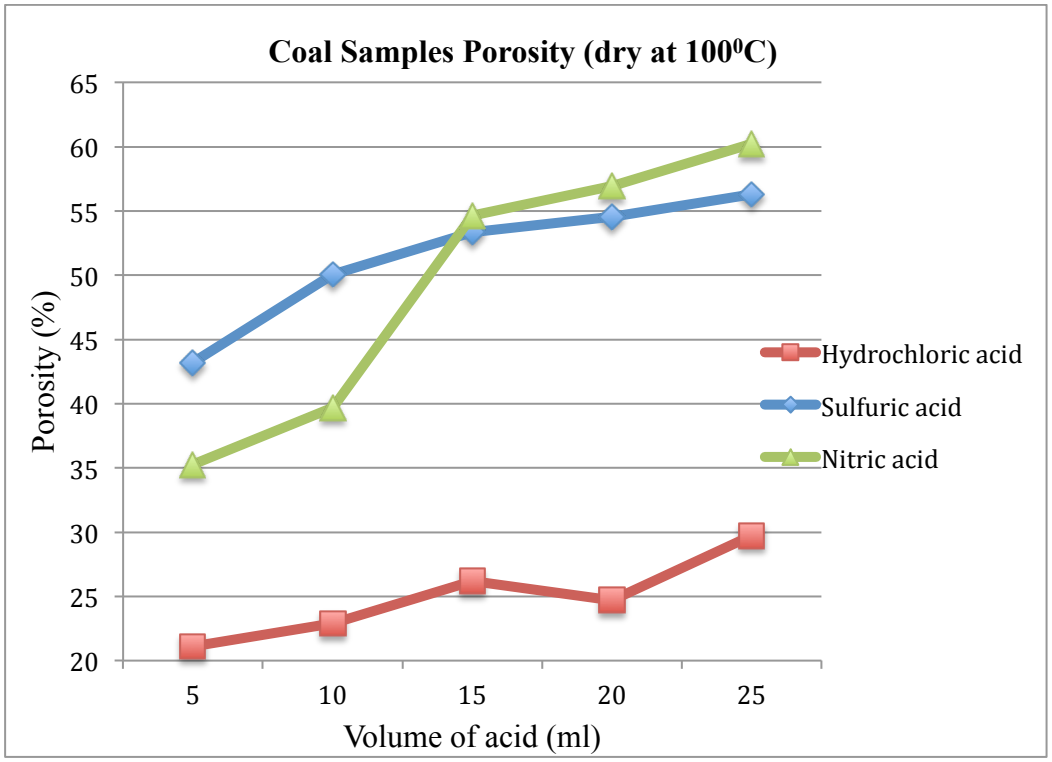


Figure 20 Graph of porosity vs volume of acid for sample dry at 100^0C

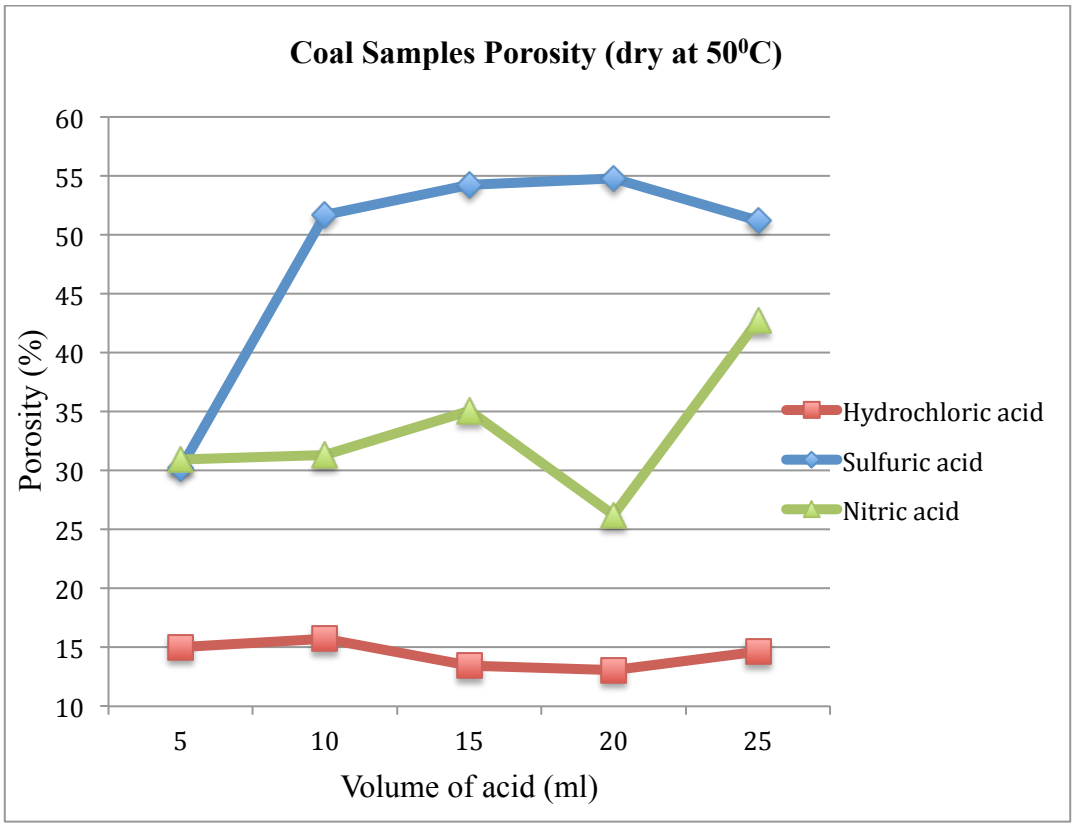


Figure 21 Graph of porosity vs volume of acid for sample dry at 50^0C

Based on the results obtained, it can be seen that acids able to alter the porosity of coal samples. At 100^0C, coal samples that have been stimulated by 5ml and 10ml of sulfuric acid gave the highest porosity percentage. At volume of 15ml, 20ml and 25ml, nitric acid shows better results on porosity percentage. Between these three acids, hydrochloric acid shows the lowest performance to alter the porosity of the samples. Based on Figure 20, drying the coal samples in oven at 100^0C, all acids able to increase the porosity of coal samples when increased the volume, except hydrochloric acid, which the porosity had decreased a bit at volume of 20ml. This may be due to the irregular size of coal samples that have been crushed and prepared. Smaller samples were dried easily compared to bigger size samples, thus the porosity calculation was affected by the weight of the samples.

On the other hand, at 50^0C, sulfuric acid gave the best results on porosity percentage, followed by nitric acid and hydrochloric acid. Based on Figure 21, the highest porosity percentage can be obtained by using 20ml of sulfuric acid and decreased at volume of 25ml. Eventhough nitric acid gave better results compared to hydrochloric

acid, but the porosity percentage for both acids were increased and decreased unevenly.

Comparing the results in both conditions (drying coal sample at 100^0C and 50^0C), it can be seen that drying coal samples at 100^0C able to give better increment on the porosity percentage. The results obtained for samples dried at 50^0C were not very encouraging and the porosity percentage increased and decreased unevenly. This suggests that, the coal samples are not totally dry when drying at lower temperature, and cause the samples to adsorb lesser acids.

From the analysis made, it can be conclude that, higher percentage of porosity can be obtained by drying the samples at higher temperature. It also depends on the type and amount of acid used. The increment of the porosity is also due to the reaction of high concentration acids with coal samples. From this experiment, at higher volume, sulfuric acid shows high possibility to increase the porosity of coal exponentially at both drying temperature (100^0C and 50^0C). Therefore, sulfuric acid is a good candidate to be used for acid stimulation in coal formation.

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

This research is focused to examine whether reaction of coal samples with acids can result in higher porosity. From the analysis made in both experiments, it is proved that the use of acid was able to give increment in coal porosity. The first experiment using Gas adsorption Column Unit, the results were analyzed in term of adsorption capacity, while for the second experiment, the results were analyzed based on the porosity calculation. Higher porosity can be obtained by stimulating the coal samples in higher volume of acids and it also depends on the type of acid used. Based on the analysis made, sulfuric acid can be concluded as the best candidate for acid stimulation in coal formation compared to hydrochloric acid and nitric acid.

On the other hand, the formula that being used in Porosity Measurements experiment was not applicable to calculate the porosity of coal. The possible recommendation is to conduct a porosity test to obtain accurate values of coal porosity. Nevertheless, future study can be made on the effect of acid on other property such as the permeability of coal.

REFERENCES

"Alberta Energy, About Coalbed Methane". Retrieved as on 5/2/2013 from website http://www.energy.alberta.ca/naturalgas/754.asp

Amani, M. & Juvkam-Wold, H.C. (1995). "Dewatering of Coalbed Methane Wells with Hydraulic Gas Pump," Paper no. SPE 030982. Presented at the SPE Eastern Regional Conference & Exhibition held in Morgantown, MV, U.S.A., 17-21 September 1995.

Bansal R.C., Donnet J.B. & Stoeckli F. (1998). "Active Carbon". Marcel Dekker Inc. (p.1)

Bansal R.C. & Goyal M. (2005). "Activated Carbon Adsorption". Taylor & Francis Group

Bell D. A., Towler B. F. & Fan M. (2011). "Coal Gasification and Its Applications". Elsevier (p. 4)

Iqbal Ahmed, Ani Idris, Ahmed Hussain, Zainal bin Abidin & Saad Khan (2013). Influence of Co-Solvent Concentration on The Properties of Dope Solution and Performance of PES Membrane. Accepted article in Press of Chemical Engineering & Technology, 1 July 2013.

Juphil A. Lamanilao (1995). Adsorption from Solutions of Acetic Acid on Charcoal. BSChE, Cebu Institute of Technology, Cebu City

"Kentucky Geological Survey, How is Coal Formed?". Retrieved as on 16/4/2013 from website http://www.uky.edu/KGS/coal/coalform.htm

Kinney, C.R. & Gray V.E. (1959). Reaction of a Bituminous Coal with Sulfuric Acid. The Pennsylvania State University. Presented before the Division of Gas and Fuel Chemistry, American Chemical Society, Boston, Massachusetts, 5-10 April 1959.

Kong Chai Chen, Sonny Irawan, Chow Weng Sum & Saleem Qadir Tunio, 2011, "Preliminary Study on Gas Storage Capacity and Gas-in-Place for CBM Potential in Balingian Coalfield, Sarawak Malaysia", *International Journal of Applied Science and Technology* **1 (2):** 82-94

Miller B. G. (2005), "Coal Energy Systems". Elsevier Academic Press (pp. 1, 2, 6)

Mohamed, A.R. & Lee, K.T., 2004. Energy Policy for Sustainable Development in Malaysia, Paper no. 9-028 (O). Prepared for presentation at The Joint International Conference on "Sustainable Energy and Environment (SEE)" held in Hua Hin, Thailand, 1-3 December 2004.

Moore, T.A., 2012, "Coalbed Methane: A review," *International Journal of Coal Geology* **101**: 36-81. Elsevier.

"Oilfield Glossary, Well Stimulation". Retrieved as on 14/2/2013 from website http://www.glossary.oilfield.slb.com/en/Terms.aspx?LookIn=term%20name&filter=well+stimulation

"Acid, Oxford Dictionaries". Retrieved as on 23/2/13 from website http://oxforddictionaries.com/definition/english/acid

Palmer, I.D., 1992. "Review of Coalbed Methane Well Stimulation," Paper no. SPE 22395, prepared for presentation at the SPE International Meeting on Petroleum Engineering held in Beijing, China, 24-27 March 1992.

Seidle, J. (2011), "Fundamentals of Coalbed Methane Reservoir Engineering". PennWell (pp.155-169)

Shi Kai-yi, Tao Xiu-xiang, Hong Fen-fen, He Huan, Ji Yong-hua and Li Ji-lan, 2012, "Mechanism of Oxidation of Low Rank Coal by Nitric Acid," *Journal of Coal Science & Engineering* **18 (4):** 396-399

Tonnsen, R.R. & Miskimins, J.L, 2011, "Simulation of Deep-Coalbed-Methane Permeability and Production Assuming Variable Pore-Volume Compressibility," *Journal of Canadian Petroleum Technology* (pp. 23-31)

US Environmental Protection Agency (June 2004). Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed Methane Reservoirs (Chapter 3, pp. 3-29).

Universiti Teknologi PETRONAS, Chemical Laboratory, "Experiment Manual: Gas Adsorption Column Unit". Received as on 14/6/2013.

Universiti Teknologi PETRONAS, Chemical Laboratory, "Fisher Scientific, Safety Data Sheet (SDS)". Received as on 18/7/2013.

Universiti Teknologi PETRONAS, Chemical Laboratory, "MERCK, Safety Data Sheet (SDS)". Received as on 14/5/2013.

Universiti Teknologi PETRONAS, Chemical Laboratory, "Price Agreement Chemicals". Received as on 10/4/2013.

Xiong, H. (August 1994). Prediction of Effective Acid Penetration and Acid Volume for Matrix Acidizing Treatments in Naturally Fractured Carbonates. SPE Production and Facilities, S.A. Holditch and Assocs. Inc. (p. 188)

Yang, Y. & Zoback, M.D., 2011. The Effects of Gas Adsorption on Swelling, Visco-plastic Creep and Permeability of Sub-bituminous Coal, Paper no. ARMA 11-433. Prepared for presentation at the 45th US Rock Mechanics/Geomechanics Symposium held in San Francisco, CA, 26-29 June 2011.

APPENDICES

Appendix 1: Technical paper